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Rec'd PCT/PT 15 DEC 2004

PCT/US 03/16944 #2

10/518120

P1 1030656

REC'D 07 JUL 2003

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FILING DATE.

APPLICATION NUMBER: 60/394,098

FILING DATE: July 05, 2002

RELATED PCT APPLICATION NUMBER: PCT/US03/16944

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# PROVISIONAL APPLICATION COVER SHEET



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This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(b)(2)

Docket No.		2002B094		Type a plus sign (+) inside this box		+
INVENTOR(S)/APPLICANTS						
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Title of the Invention (280 characters max)						
Functionalized Elastomer Nanocomposite						
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State:		Texas		Zip Code	77522	Country
						US
Enclosed Application Parts (check all that apply)						
<input checked="" type="checkbox"/> Specification		Number of Pages [ 46 ]		<input type="checkbox"/> Small Entity Statement		
<input type="checkbox"/> Drawings		Number of Sheets [ ]		<input type="checkbox"/> Other (specify)		
Method of Payment						
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees and credit Deposit Account No. 05-1715.				Provisional Filing Fee Amount \$ 160.00		

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.



No



Yes, the name of the U.S. Government Agency and the Government Contract Number are:

Respectfully submitted,

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July 5, 2002

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## PROVISIONAL APPLICATION FILING ONLY

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**TITLE: FUNCTIONALIZED ELASTOMER NANOCOMPOSITE****FIELD OF THE INVENTION**

5 The present invention relates to nanocomposites comprising clays and elastomers. More particularly, the present invention relates to nanocomposites suitable for air barriers that are a blend of a clay and a functionalized phenyl-containing, or styrenic-based, elastomer, wherein the functionalization may be carried out via Friedel-Crafts reaction.

**10 BACKGROUND OF THE INVENTION**

Nanocomposites are polymer systems containing inorganic particles with at least one dimension in the nanometer range. Elastomers comprising phenyl groups including, for example, styrenic-based elastomers comprising at least one styrene or substituted styrene unit therein, are one type of elastomer that can be  
15 incorporated into a nanocomposite. Some examples of these are disclosed in US 6,060,549, 6,103,817, 6,034,164, 5,973,053, 5,936,023, 5,883,173, 5,807,629, 5,665,183, 5,576,373, and 5,576,372. A common type of inorganic particle used in nanocomposites are phyllosilicates, an inorganic substance from the general class of so called "nano-clays" or "clays". Ideally, intercalation should take place  
20 in the nanocomposite, wherein the polymer inserts into the space or gallery between the clay surfaces. Ultimately, it is desirable to have exfoliation, wherein the polymer is fully dispersed with the individual nanometer-size clay platelets. Due to the general enhancement in air barrier qualities of various polymer blends when clays are present, there is a desire to have a nanocomposite with low air  
25 permeability; especially a dynamically vulcanized elastomer nanocomposite such as used in the manufacture of tires.

One method to improve nanocomposite performance is to use functionalized polymers blended with clay. This approach has been limited to  
30 materials that are soluble in water or to materials that can be incorporated into the polymerization reaction. This approach has been used to prepare nylon nanocomposites, using for example, oligomeric and monomeric caprolactam as

the modifier. Polyolefin nanocomposites, such as polypropylene nanocomposites, have utilized maleic anhydride grafted polypropylenes to achieve some success in the formation of nanocomposites.

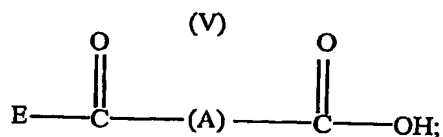
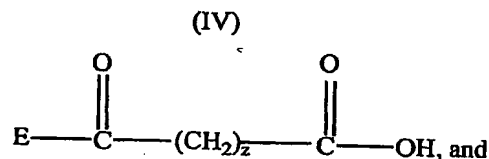
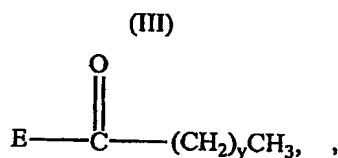
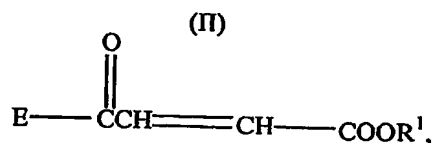
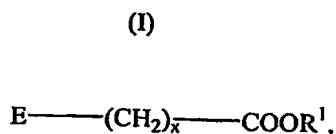
5 To form articles such as air barriers, it is desirable to use elastomers such as isobutylene-based elastomers, for example, poly(isobutylene-*co-p*-alkylstyrene) elastomers and poly(isobutylene-*co*-isoprene) elastomers. While these elastomers have been functionalized in order to improve compatibility or cross-linkability with other polymers, suitability of such functionalized polymers for  
10 nanocomposites has not been demonstrated or disclosed. See, for example, US 6,372,855 B1; 6,015,862; 5,849,828; 5,480,810; 5,814,707; 5,700,871; 5,498,673; 5,356,950; JP 11323023 (98 JP-130725 A); EP 0 787 157 B1; and *Liu et al.*, 43 POLYMER BULLETIN 51-58 (1999). What would be desirable is to provide an improved air barrier using such nanomposites that include these styrenic-based  
15 elastomers, thus improving upon the air barrier qualities that exist for these elastomers.

#### SUMMARY OF THE INVENTION

The present invention provides a nanocomposite comprising suitable for  
20 air barrier applications, the nanocomposite comprising a blend of clay and an elastomer comprising C<sub>2</sub> to C<sub>10</sub> olefin derived units; wherein the elastomer also comprises functionalized monomer units pendant to the elastomer. Desirable embodiments of the elastomer include poly(isobutylene-*co-p*-alkylstyrene) elastomers and ethylene-propylene-alkylstyrene rubber, which are functionalized  
25 via Friedel-Crafts reaction with a Lewis acid and a functionalizing agent such as acid anhydrides and/or acylhalides. The clay is exfoliated in one embodiment by the addition of exfoliating agents such as alkyl amines and silanes to the clay. The composition can include secondary rubbers such as general purpose rubbers, and curatives, fillers, and the like. The nanocomposites of the invention have  
30 improved air barrier properties such as are useful for tire innerliners and innertubes.

# **DETAILED DESCRIPTION OF THE INVENTION**

The present invention provides a nanocomposite material suitable for air barriers such as innerliners and innertubes for transportation vehicles, trucks, automobiles, and the like. In one aspect of the invention, the nanocomposite comprises clay, preferably swellable clay, and more preferably exfoliated clay, and an elastomer comprising C<sub>2</sub> to C<sub>10</sub> olefin derived units (which includes isoolefin derived units); wherein the elastomer also comprises functionalized monomer units described by the following groups (I), (II), (III), (IV) and (V) pendant to the elastomer, E:



10

wherein R<sup>1</sup> is selected from hydrogen, C<sub>1</sub> to C<sub>20</sub> alkyls, alkenyls or aryls, substituted C<sub>1</sub> to C<sub>20</sub> alkyls, alkenyls or aryls; wherein the value of x ranges from 0 to 20, preferably from 1 to 10, and more preferably from 1 to 5; and wherein the value of y ranged from 0 to 20, preferably from 0 to 10; and wherein the value of z ranges from 1 to 20, preferably from 1 to 10, and more preferably from 1 to 5; and wherein "A" is selected from an alkyl, alkenyl, and aryl group, any of which are either substituted or not.

Alternately, the nanocomposite of the present invention can be described as blend of clay and the reaction product of contacting an elastomer comprising C<sub>2</sub>

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to C<sub>10</sub> olefin derived units, an grafting promoter such as, for example, a Lewis acid, and at least one functionalizing compound, such as, for example, an acid anhydride, acylhalide, or blend thereof. In any case, the clay may be a swellable clay in one embodiment, or an exfoliated clay in another embodiment, wherein the  
5 clay is exfoliated with an exfoliating additive such as an amine or silane compound, as described herein.

The elastomer may be any suitable elastomer as described herein, desirably isobutylene elastomers such as poly(isobutylene-*co-p*-alkylstyrene)  
10 elastomers and EP rubber such as poly(ethylene-*co*-propylene-*co*-methylstyrene). These are described further below. The nanocomposite may also include other secondary rubbers, fillers, and curatives, and may be cured by such means as, for example, heating, to form an article of manufacture that is suitable for air barriers, etc.

15 The various aspects of the nanocomposite and its use as an air barrier are described more particularly herein, wherein the various embodiments described for each component are attributable to the various aspects and embodiments of the invention.

20 As used herein, in reference to Periodic Table "Groups", the new numbering scheme for the Periodic Table Groups are used as in HAWLEY'S CONDENSED CHEMICAL DICTIONARY 852 (13th ed. 1997).

25 The term "elastomer", as used herein, refers to any polymer or composition of polymers consistent with the ASTM D1566 definition. The term "elastomer" may be used interchangeably with the term "rubber", as used herein.

30 As used herein, the term "alkyl" refers to a paraffinic hydrocarbon group which may be derived from an alkane by dropping one or more hydrogens from the formula, such as, for example, a methyl group, or CH<sub>3</sub><sup>-</sup>, or an ethyl group, CH<sub>3</sub>CH<sub>2</sub><sup>-</sup>, etc.

As used herein, the term "alkenyl" refers to an unsaturated paraffinic hydrocarbon group which may be derived from an alkane by dropping one or more hydrogens from the formula, such as, for example, an ethenyl group,  $\text{CH}_2=\text{CH}^-$ , and a propenyl group, or  $\text{CH}_3\text{CH}=\text{CH}^-$ , etc.

As used herein, the term "aryl" refers to a hydrocarbon group that forms a ring structure characteristic of aromatic compounds such as, for example, benzene, naphthalene, phenanthrene, anthracene, etc., and typically possess alternate double bonding ("unsaturation") within its structure. An aryl group is thus a group derived from an aromatic compound by dropping one or more hydrogens from the formula such as, for example, phenyl, or  $\text{C}_6\text{H}_5^-$ .

By "substituted", it is meant substitution of at least one hydrogen group by at least one substituent selected from, for example, halogen (chlorine, bromine, fluorine, or iodine), amino, nitro, sulfoxy (sulfonate or alkyl sulfonate), thiol, alkylthiol, and hydroxy; alkyl, straight or branched chain having 1 to 20 carbon atoms which includes methyl, ethyl, propyl, tert-butyl, isopropyl, isobutyl, etc.; alkoxy, straight or branched chain alkoxy having 1 to 20 carbon atoms, and includes, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, secondary butoxy, tertiary butoxy, pentyloxy, isopentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, and decyloxy; haloalkyl, which means straight or branched chain alkyl having 1 to 20 carbon atoms which is substituted by at least one halogen, and includes, for example, chloromethyl, bromomethyl, fluoromethyl, iodomethyl, 2-chloroethyl, 2-bromoethyl, 2-fluoroethyl, 3-chloropropyl, 3-bromopropyl, 3-fluoropropyl, 4-chlorobutyl, 4-fluorobutyl, dichloromethyl, dibromomethyl, difluoromethyl, diiodomethyl, 2,2-dichloroethyl, 2,2-dibromomethyl, 2,2-difluoroethyl, 3,3-dichloropropyl, 3,3-difluoropropyl, 4,4-dichlorobutyl, 4,4-difluorobutyl, trichloromethyl, 4,4-difluorobutyl, trichloromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, 2,3,3-trifluoropropyl, 1,1,2,2-tetrafluoroethyl, and 2,2,3,3-

tetrafluoropropyl. Thus, for example, an example of a "substituted styrenic unit" would include *p*-methylstyrene, *p*-ethylstyrene, etc.

#### Elastomer

5           Elastomers suitable for use in the present invention comprise C<sub>2</sub> to C<sub>10</sub> olefin derived units. As used herein, the term "olefin" includes "isoolefins" such as, for example, isobutylene, as well as "multiolefins" such as, for example, isoprene. Preferably, the elastomer also comprises monomer units having phenyl groups pendant to the elastomer backbone, the phenyl groups either substituted or  
10   not. More preferably, the elastomer also comprises styrenic derived units selected from styrenes and substituted styrenes, non-limiting examples of which include  $\alpha$ -methylstyrene, *o*- (ortho), *m*- (meta), and *p* (para)-methylstyrene, *o*-, *m*-, and *p*-tert-butylstyrene, etc.

15           In one embodiment of the invention, the elastomer is a random copolymer of units selected from C<sub>2</sub> to C<sub>10</sub> olefin derived units (hereinafter, ethylene or "C<sub>2</sub>" is referred to as an olefin derived unit) and styrenic derived unit such as, for example *p*-alkylstyrene derived units; wherein the *p*-alkylstyrene derived units are preferably *p*-methylstyrene containing at least 80%, more preferably at least 90%  
20   by weight of the *p*-isomer. In another embodiment of the invention, the elastomer is a random copolymer of a C<sub>4</sub> to C<sub>7</sub> isoolefin, such as isobutylene, and a styrenic monomer, such as a *p*-alkylstyrene comonomer, preferably *p*-methylstyrene containing at least 80%, more preferably at least 90% by weight of the *p*-isomer. In yet another embodiment, the elastomer is a copolymer of an isoolefin such as  
25   isobutylene and a multiolefin such as isoprene, or "butyl" rubber.

          In one embodiment of the invention, the elastomer may be a copolymer of styrenic derived units and/or substituted styrenic derived units, and olefin derived units as described above. The styrene derived units are present from 3 wt% to 20  
30   wt% based on the total weight of the polymer in one embodiment, from 5 wt% to 12 wt% in another embodiment, from 5 wt% to 15 wt% in yet another embodiment, and from 8 wt% to 13 wt% in yet another embodiment, wherein a



desirable range of styrene derived unit may include any upper wt% limit with any lower wt% limit described herein. The olefin is present in the elastomer in a range of from 70 wt% to 99.5 wt% by weight of the elastomer in one embodiment, and 85 wt% to 99.5 wt% in another embodiment. Suitable olefins are selected from C<sub>2</sub> to C<sub>10</sub> olefins, non-limiting examples of which include ethylene, propene, 1-butene, isobutylene (an isoolefin), 1-hexene, 1-octene, cyclopentadiene (a multiolefin) and isoprene (a multiolefin). For example, one embodiment of a suitable elastomer for nanocomposites of the invention may be a copolymer or terpolymer of any one or two of these monomers with a styrenic monomer such as, for example,  $\alpha$ -methylstyrene, *o*-methylstyrene, *m*-methylstyrene, and *p*-methylstyrene monomers.

Non-limiting examples of elastomers that are suitable for the nanocomposite of the invention include any one or a mixture of natural rubber, poly(isobutylene-*co*-isoprene), polybutadiene, poly(styrene-*co*-butadiene), poly(isoprene-*co*-butadiene), poly(styrene-isoprene-butadiene), poly(isoprene-isobutylene-alkylstyrene), star-branched polyisobutylene rubber, poly(isobutylene-*co*-*p*-methylstyrene), ethylene-propylene-alkylstyrene rubber, ethylene-propylene-styrene rubber, wherein reference to an "alkyl" includes any C<sub>1</sub> to C<sub>10</sub> straight or branched chain alkyl.

In one embodiment of the invention, the elastomer suitable for the nanocomposite is a non-halogenated elastomer, meaning that the elastomer has not been subjected to a halogenation process, or otherwise comprise halogen moieties.

An example of a suitable elastomer for use in the present invention is poly(isobutylene-*co*-*p*-methylstyrene), or "XP50" (ExxonMobil Chemical Company, Houston TX). These isoolefin copolymers, their method of preparation and cure are more particularly disclosed in US 5,162,445. These elastomers have a substantially homogeneous compositional distribution such that at least 95% by weight of the polymer has a *p*-alkylstyrene content within 10% of the average *p*-

alkylstyrene content of the polymer. Desirable copolymers are also characterized by a molecular weight distribution ( $M_w/M_n$ ) of between 2 and 20 in one embodiment, and less than 10 in another embodiment, and less than 5 in another embodiment, and less than 2.5 in yet another embodiment, and greater than 2 in yet another embodiment; a preferred viscosity average molecular weight in the range of from 200,000 up to 2,000,000 and a preferred number average molecular weight in the range of from 25,000 to 750,000 as determined by gel permeation chromatography.

10 The "elastomer", as described herein, may also comprise a composition of one or more of the same elastomer having differing molecular weights to yield a composition having a bimodal molecular weight distribution. This bimodal distribution can be achieved by, for example, having a low molecular weight component in the elastomer. This can be accomplished by physically blending  
15 two different MW polymers together, or by *in situ* reactor blending. In one embodiment, the elastomer has a low molecular weight (weight average molecular weight) component of from 5,000 MW to 80,000 MW in one embodiment, and from 10,000 MW to 60,000 MW in another embodiment; the low molecular weight component comprising from 5 to 40 wt% of the composition in one  
20 embodiment, and from 10 to 30 wt% of the composition in another embodiment.

In an embodiment comprising poly(isobutylene-*co-p*-methylstyrene) as the elastomer, the *p*-methylstyrene derived units are present from 3 wt% to 15 wt% based on the total weight of the polymer, and from 5 wt% to 12 wt% in another  
25 embodiment, and from 8 wt% to 13 wt% in yet another embodiment, wherein a desirable range of *p*-methylstyrene may include any upper wt% limit with any lower wt% limit described herein. The isobutylene derived units are present in the elastomer in a range from 70 to 99.5 wt% by weight of the elastomer in one embodiment, and 85 to 99.5 wt% in another embodiment.

30

In another embodiment, the elastomer suitable for use in the nanocomposite of the invention is a copolymer of an isomonoolefin (or isoolefin)

and a multiolefin, or a "butyl" rubber. In one embodiment of the invention, the elastomer is a copolymer of a C<sub>4</sub> to C<sub>6</sub> isoolefin and a multiolefin. In another embodiment, the elastomer is a blend of a polydiene or block copolymer, and a copolymer of a C<sub>4</sub> to C<sub>6</sub> isoolefin and a conjugated, or a "star-branched" butyl polymer. The butyl elastomer useful in the present invention can thus be described as comprising C<sub>4</sub> to C<sub>7</sub> isoolefin derived units and multiolefin derived units, and includes both "butyl rubber" and so called "star-branched" butyl rubber.

As used herein, "butyl rubber" refers to both butyl rubber and so-called "star-branched" butyl rubber, described below. Preferably, the olefin polymerization feeds employed in producing the butyl rubber of the invention are those olefinic compounds conventionally used in the preparation of butyl-type rubber polymers. Butyl polymers may be prepared by reacting a comonomer mixture, the mixture having at least (1) a C<sub>4</sub> to C<sub>6</sub> isoolefin monomer component such as isobutylene with (2) a multiolefin, or conjugated diene, monomer component. The isoolefin is in a range from 70 wt% to 99.5 wt% by weight of the total comonomer mixture in one embodiment, and 85 wt% to 99.5 wt% in another embodiment. The multiolefin component in one embodiment is present in the comonomer mixture from 30 to 0.5 wt% in one embodiment, and from 15 wt% to 0.5 wt% in another embodiment. In yet another embodiment, from 8 wt% to 0.5 wt% of the comonomer mixture is multiolefin.

Suitable isoolefins include C<sub>4</sub> to C<sub>7</sub> compounds such as isobutylene, isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 4-methyl-1-pentene. The multiolefin is a C<sub>4</sub> to C<sub>14</sub> conjugated diene such as isoprene, butadiene, 2,3-dimethyl-1,3-butadiene, myrcene, 6,6-dimethyl-fulvene, cyclopentadiene, hexadiene and piperylene. One embodiment of a butyl rubber suitable for use in the invention comprises from 92 wt% to 99.5 wt% of isobutylene and from 0.5 wt% to 8 wt% isoprene, and from 95 wt% to 99.5 wt% isobutylene and 0.5 wt% to 5.0 wt% isoprene in yet another embodiment.

The star-branched butyl rubber is a composition of a butyl rubber, either halogenated or not, and a polydiene or block copolymer, either halogenated or not. The polydienes/block copolymer, or branching agents (hereinafter "polydienes"), are typically cationically reactive and are present during the polymerization of the butyl rubber, or can be blended with the butyl or butyl rubber to form the star-branched butyl rubber.

More particularly, star-branched butyl rubber is typically a composition of the butyl and a copolymer of a polydiene and a partially hydrogenated polydiene selected from the group including styrene, polybutadiene, polyisoprene, polypiperylene, natural rubber, styrene-butadiene rubber, ethylene-propylene diene rubber, styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers. These polydienes are present, based on the monomer wt%, greater than 0.3 wt% in one embodiment, and from 0.3 wt% to 3 wt% in another embodiment, and from 0.4 wt% to 2.7 wt% in yet another embodiment.

The elastomer or functionalized elastomer is present in the nanocomposite of the invention from 10 to 100 phr in one embodiment, from 20 to 80 phr in another embodiment, and from 30 to 70 phr in yet another embodiment, wherein a desirable range may be any combination of any upper phr limit with any lower phr limit.

#### Clay

Compositions of the invention include at least one functionalized elastomer blended by any suitable means with at least one clay, a swellable clay in one embodiment, which may or may not be exfoliated using an exfoliating agent. Swellable clay materials suitable for the purposes of this invention include natural or synthetic phyllosilicates, particularly smectic clays such as montmorillonite, nontronite, beidellite, volkonskoite, laponite, hectorite, saponite, sauconite, magadite, kenyaite, stevensite and the like, as well as vermiculite, halloysite, aluminate oxides, hydrotalcite and the like. These swellable clays generally comprise particles containing a plurality of silicate platelets having a thickness of

8-12Å, and contain exchangeable cations such as  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{K}^+$  or  $\text{Mg}^{+2}$  present at the interlayer surfaces.

The swellable clay may be exfoliated by treatment with organic molecules  
5 (swelling or exfoliating "agents" or "additives") capable of undergoing ion exchange reactions with the cations present at the interlayer surfaces of the layered silicate. Suitable exfoliating agents include cationic surfactants such as ammonium, alkylamines or alkylammonium (primary, secondary, tertiary and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or  
10 arylaliphatic amines, phosphines and sulfides. Desirable amine compounds (or the corresponding ammonium ion) are those with the structure  $\text{R}^2\text{R}^3\text{R}^4\text{N}$ , wherein  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are  $\text{C}_1$  to  $\text{C}_{30}$  alkyls or alkenes in one embodiment,  $\text{C}_1$  to  $\text{C}_{20}$  alkyls or alkenes in another embodiment, which may be the same or different. In one embodiment, the exfoliating agent is a so called long chain tertiary amine, wherein  
15 at least  $\text{R}^2$  is a  $\text{C}_{14}$  to  $\text{C}_{20}$  alkyl or alkene.

Another class of exfoliating agents include those which can be covalently bonded to the interlayer surfaces. These include polysilanes of the structure -  
20  $\text{Si}(\text{R}^5)_2\text{R}^6$  where  $\text{R}^5$  is the same or different at each occurrence and is selected from alkyl, alkoxy or oxysilane and  $\text{R}^6$  is an organic radical compatible with the matrix polymer of the composite.

Other suitable exfoliating agents include protonated amino acids and salts thereof containing 2-30 carbon atoms such as 12-aminododecanoic acid, epsilon-caprolactam and like materials. Suitable swelling agents and processes for  
25 intercalating layered silicates are disclosed in US 4,472,538, 4,810,734, 4,889,885 as well as WO92/02582.

In one embodiment, the exfoliating agents includes all primary, secondary  
30 and tertiary amines and phosphines; alkyl and aryl sulfides and thiols; and their polyfunctional versions. Desirable additives include: long-chain tertiary amines such as N,N-dimethyl-octadecylamine, N,N-dioctadecyl-methylamine, so called

dihydrogenated tallowalkyl-methylamine and the like, and amine-terminated polytetrahydrofuran; long-chain thiol and thiosulfate compounds like hexamethylene sodium thiosulfate.

5       The exfoliating additive such as described herein is present in the composition in an amount to achieve optimal air retention as measured by the permeability testing described herein. For example, the additive may be present from 0.1 to 20 phr in one embodiment, and from 0.2 to 15 phr in another embodiment, and from 0.3 to 10 phr in yet another embodiment. The exfoliating  
10   agent, if present, may be added to the composition at any stage; for example, the additive may be added to the interpolpolymer, followed by addition of the clay, or may be added to the elastomer and clay mixture; or the additive may be first blended with the clay, followed by blending with the interpolpolymer in yet another embodiment.

15       In another embodiment of the invention, improved elastomer impermeability is achieved by the presence of at least one polyfunctional curative. An embodiment of such polyfunctional curatives can be described by the formula  $Z-R^7-Z'$ , wherein  $R^7$  is one of a  $C_1$  to  $C_{15}$  alkyl,  $C_2$  to  $C_{15}$  alkenyl, and  $C_6$  to  $C_{12}$   
20   cyclic aromatic moiety, substituted or unsubstituted; and Z and Z' are the same or different and are one of a thiosulfate group, mercapto group, aldehyde group, carboxylic acid group, peroxide group, alkenyl group, or other similar group that is capable of crosslinking, either intermolecularly or intramolecularly, one or more  
25   strands of a polymer having reactive groups such as unsaturation. So-called bis-thiosulfate compounds are an example of a desirable class of polyfunctional compounds included in the above formula. Non-limiting examples of such polyfunctional curatives are as hexamethylene bis(sodium thiosulfate) and hexamethylene bis(cinnamaldehyde), and others are well known in the rubber  
30   compounding arts. These and other suitable agents are disclosed in, for example, the BLUE BOOK, MATERIALS, COMPOUNDING INGREDIENTS, MACHINERY AND SERVICES FOR RUBBER (Don. R. Smith, ed., Lippincott & Petto Inc. 2001). The

polyfunctional curative, if present, may be present in the composition from 0.1 to 8 phr in one embodiment, and from 0.2 to 5 phr in yet another embodiment.

5 Treatment with the exfoliating agents described above results in intercalation or "exfoliation" of the layered platelets as a consequence of a reduction of the ionic forces holding the layers together and introduction of molecules between layers which serve to space the layers at distances of greater than 4Å, preferably greater than 9Å. This separation allows the layered silicate to more readily sorb polymerizable monomer material and polymeric material  
10 between the layers and facilitates further delamination of the layers when the intercalate is shear mixed with matrix polymer material to provide a uniform dispersion of the exfoliated layers within the polymer matrix.

The amount of clay or exfoliated clay incorporated in the nanocomposites  
15 in accordance with an embodiment of the invention is sufficient to develop an improvement in the mechanical properties and barrier properties of the nanocomposite, for example, tensile strength or oxygen permeability. Amounts generally will range from 0.1 wt% to 50 wt% in one embodiment, and from 0.5 wt% to 10 wt% in another embodiment, and from 0.5 wt% to 15 wt% in another  
20 embodiment, and from 1 wt% to 30 wt% in yet another embodiment, and from 1 wt% to 5 wt% in yet another embodiment, based on the polymer content of the nanocomposite. Expressed in parts per hundred rubber, the clay or exfoliated clay may be present from 1 to 30 phr in one embodiment, and from 5 to 20 phr in another embodiment. In one embodiment, the exfoliated clay is an alkylamine-  
25 exfoliated clay.

### Secondary Rubber Component

A secondary rubber, or "general purpose rubber" component may be present in compositions and end use articles of the present invention. These  
30 rubbers may be blended by any suitable means with the elastomer or elastomer/clay composition. These rubbers include, but are not limited to, natural rubbers, polyisoprene rubber, poly(styrene-co-butadiene) rubber (SBR),

polybutadiene rubber (BR), poly(isoprene-*co*-butadiene) rubber (IBR), styrene-isoprene-butadiene rubber (SIBR), ethylene-propylene rubber (EPM), ethylene-propylene-diene rubber (EPDM), polysulfide, nitrile rubber, propylene oxide polymers, star-branched butyl rubber and halogenated star-branched butyl rubber, brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; poly(isobutylene-*co-p*-methylstyrene) and halogenated poly(isobutylene-*co-p*-methylstyrene), such as, for example, terpolymers of isobutylene derived units, *p*-methylstyrene derived units, and *p*-bromomethylstyrene derived units, and mixtures thereof.

A desirable embodiment of the secondary rubber component present is natural rubber. Natural rubbers are described in detail by *Subramaniam* in RUBBER TECHNOLOGY 179-208 (Maurice Morton, ed., Chapman & Hall 1995). Desirable embodiments of the natural rubbers of the present invention are selected from Malaysian rubber such as SMR CV, SMR 5, SMR 10, SMR 20, and SMR 50 and mixtures thereof, wherein the natural rubbers have a Mooney viscosity at 100°C (ML 1+4) of from 30 to 120, more preferably from 40 to 65. The Mooney viscosity test referred to herein is in accordance with ASTM D-1646.

20

Polybutadiene (BR) rubber is another desirable secondary rubber useful in the composition of the invention. The Mooney viscosity of the polybutadiene rubber as measured at 100°C (ML 1+4) may range from 35 to 70, from 40 to about 65 in another embodiment, and from 45 to 60 in yet another embodiment. Some commercial examples of these synthetic rubbers useful in the present invention are NATSYN™ (Goodyear Chemical Company), and BUDENE™ 1207 or BR 1207 (Goodyear Chemical Company). A desirable rubber is high *cis*-polybutadiene (*cis*-BR). By "*cis*-polybutadiene" or "high *cis*-polybutadiene", it is meant that 1,4-*cis* polybutadiene is used, wherein the amount of *cis* component is at least 95%. An example of high *cis*-polybutadiene commercial products used in the composition BUDENE™ 1207.



Rubbers of ethylene and propylene derived units such as EPM and EPDM are also suitable as secondary rubbers. Examples of suitable comonomers in making EPDM are ethylidene norbornene, 1,4-hexadiene, dicyclopentadiene, as well as others. These rubbers are described in RUBBER TECHNOLOGY 260-283  
5 (1995). A suitable ethylene-propylene rubber is commercially available as VISTALON™ (ExxonMobil Chemical Company, Houston TX).

In another embodiment, the secondary rubber is a halogenated rubber as part of the terpolymer composition. The halogenated butyl rubber is brominated  
10 butyl rubber, and in another embodiment is chlorinated butyl rubber. General properties and processing of halogenated butyl rubbers are described in THE VANDERBILT RUBBER HANDBOOK 105-122 (Robert F. Ohm ed., R.T. Vanderbilt Co., Inc. 1990), and in RUBBER TECHNOLOGY 311-321 (1995). Butyl rubbers, halogenated butyl rubbers, and star-branched butyl rubbers are described by  
15 *Edward Kresge and H.C. Wang* in 8 KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY 934-955 (John Wiley & Sons, Inc. 4th ed. 1993).

The secondary rubber component of the present invention includes, but is not limited to at least one or more of brominated butyl rubber, chlorinated butyl  
20 rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; halogenated poly(isobutylene-*co-p*-methylstyrene), such as, for example, terpolymers of isobutylene derived units, *p*-methylstyrene derived units, and *p*-bromomethylstyrene derived units (BrIBMS), and the like halomethylated aromatic interpolymers as in US 5,162,445; US  
25 4,074,035; and US 4,395,506; halogenated isoprene and halogenated isobutylene copolymers, polychloroprene, and the like, and mixtures of any of the above. Some embodiments of the halogenated rubber component are also described in US 4,703,091 and US 4,632,963.

30 In one embodiment of the invention, a so called semi-crystalline copolymer ("SCC") is present as the secondary "rubber" component. Semi-crystalline copolymers are described in WO 00/69966. Generally, the SCC is a

copolymer of ethylene or propylene derived units and  $\alpha$ -olefin derived units, the  $\alpha$ -olefin having from 4 to 16 carbon atoms in one embodiment, and in another embodiment the SCC is a copolymer of ethylene derived units and  $\alpha$ -olefin derived units, the  $\alpha$ -olefin having from 4 to 10 carbon atoms, wherein the SCC has  
5 some degree of crystallinity. In a further embodiment, the SCC is a copolymer of 1-butene derived units and another  $\alpha$ -olefin derived unit, the other  $\alpha$ -olefin having from 5 to 16 carbon atoms, wherein the SCC also has some degree of crystallinity. The SCC can also be a copolymer of ethylene and styrene.

10 The secondary rubber component of the elastomer composition may be present in a range from up to 90 phr in one embodiment, from up to 50 phr in another embodiment, from up to 40 phr in another embodiment, and from up to 30 phr in yet another embodiment. In yet another embodiment, the secondary rubber is present from at least 2 phr, and from at least 5 phr in another embodiment, and  
15 from at least 5 phr in yet another embodiment, and from at least 10 phr in yet another embodiment. A desirable embodiment may include any combination of any upper phr limit and any lower phr limit. For example, the secondary rubber, either individually or as a blend of rubbers such as, for example NR and BR, may be present from 5 phr to 90 phr in one embodiment, and from 10 to 80 phr in  
20 another embodiment, and from 30 to 70 phr in yet another embodiment, and from 40 to 60 phr in yet another embodiment, and from 5 to 50 phr in yet another embodiment, and from 5 to 40 phr in yet another embodiment, and from 20 to 60 phr in yet another embodiment, and from 20 to 50 phr in yet another embodiment, the chosen embodiment depending upon the desired end use application of the  
25 composition.

The elastomeric composition may have one or more filler components such as, for example, calcium carbonate, silica, talc, titanium dioxide, and carbon black. In one embodiment, the filler is carbon black or modified carbon black,  
30 and combinations of any of these. In another embodiment, the filler is a blend of carbon black and silica. The preferred filler for such articles as tire treads and sidewalls is reinforcing grade carbon black present at a level of from 10 to 100 phr

of the blend, more preferably from 30 to 80 phr in another embodiment, and from 50 to 80 phr in yet another embodiment. Useful grades of carbon black, as described in RUBBER TECHNOLOGY, 59-85, range from N110 to N990. More desirably, embodiments of the carbon black useful in, for example, tire treads are  
5 N229, N351, N339, N220, N234 and N110 provided in ASTM (D3037, D1510, and D3765). Embodiments of the carbon black useful in, for example, sidewalls in tires, are N330, N351, N550, N650, N660, and N762.

The fillers of the present invention may be any size and typically range, for  
10 example, from about 0.0001  $\mu\text{m}$  to about 100  $\mu\text{m}$ . As used herein, silica is meant to refer to any type or particle size silica or another silicic acid derivative, or silicic acid, processed by solution, pyrogenic or the like methods and having a surface area, including untreated, precipitated silica, crystalline silica, colloidal silica, aluminum or calcium silicates, fumed silica, and the like.

15

One or more crosslinking agents are preferably used in the elastomeric compositions of the present invention, especially when silica is the primary filler, or is present in combination with another filler. More preferably, the coupling agent may be a bifunctional organosilane crosslinking agent. An "organosilane  
20 crosslinking agent" is any silane coupled filler and/or crosslinking activator and/or silane reinforcing agent known to those skilled in the art including, but not limited to, vinyl triethoxysilane, vinyl-tris-(beta-methoxyethoxy)silane, methacryloylpropyltrimethoxysilane, gamma-amino-propyl triethoxysilane (sold commercially as A1100 by Witco), gamma-mercaptopropyltrimethoxysilane  
25 (A189 by Witco) and the like, and mixtures thereof. In one embodiment, bis-(3-triethoxysilylpropyl)tetrasulfide (sold commercially as "Si69") is employed.

A processing aid may also be present in the composition of the invention. Processing aids include, but are not limited to, plasticizers, tackifiers, extenders,  
30 chemical conditioners, homogenizing agents and peptizers such as mercaptans, petroleum and vulcanized vegetable oils, mineral oils, paraffinic oils, polybutene oils, naphthenic oils, aromatic oils, waxes, resins, rosins, and the like. The aid is

typically present from 1 to 70 phr in one embodiment, from 3 to 60 phr in another embodiment, and from 5 to 50 phr in yet another embodiment. Some commercial examples of processing aids are SUNDEX™ (Sun Chemicals), a naphthenic processing oil, PARAPOL™ (ExxonMobil Chemical Company), a polybutene  
5 processing oil having a number average molecular weight of from 800 to 3000, and FLEXON™ (ExxonMobil Chemical Company), a paraffinic petroleum oil.

The compositions produced in accordance with the present invention typically contain other components and additives customarily used in rubber mixes,  
10 such as effective amounts of other nondiscolored and nondiscoloring processing aids, pigments, accelerators, crosslinking and curing materials, antioxidants, antiozonants. General classes of accelerators include amines, guanidines, thioureas, thiazoles, thiurams, sulfenamides, sulfenimides, thiocarbamates, xanthates, and the like. Crosslinking and curing agents include sulfur, zinc oxide,  
15 and fatty acids. Peroxide cure systems may also be used. The components, and other curatives, are typically present from 0.1 to 10 phr in the composition.

Generally, polymer blends, for example, those used to produce tires, are crosslinked. It is known that the physical properties, performance characteristics,  
20 and durability of vulcanized rubber compounds are directly related to the number (crosslink density) and type of crosslinks formed during the vulcanization reaction. (See, e.g., Helt et al., *The Post Vulcanization Stabilization for NR* in RUBBER WORLD, 18-23 (1991). Generally, polymer blends may be crosslinked by adding curative molecules, for example sulfur, metal oxides, organometallic compounds,  
25 radical initiators, etc., followed by heating. In particular, the following metal oxides are common curatives that will function in the present invention: ZnO, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, CrO<sub>3</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, and NiO. These metal oxides can be used alone or in conjunction with the corresponding metal fatty acid complex (e.g., zinc stearate, calcium stearate, etc.), or with the organic and fatty acids added alone, such as stearic  
30 acid, and optionally other curatives such as sulfur or a sulfur compound, an alkylperoxide compound, diamines or derivatives thereof (e.g., DIAK products sold by DuPont). (See also, *Formulation Design and Curing Characteristics of NBR*

*Mixes for Seals*, RUBBER WORLD 25-30 (1993). This method of curing elastomers may be accelerated and is often used for the vulcanization of elastomer blends.

The acceleration of the cure process is accomplished in the present invention by adding to the composition an amount of an accelerant, often an organic compound. The mechanism for accelerated vulcanization of natural rubber involves complex interactions between the curative, accelerator, activators and polymers. Ideally, all of the available curative is consumed in the formation of effective crosslinks which join together two polymer chains and enhance the overall strength of the polymer matrix. Numerous accelerators are known in the art and include, but are not limited to, the following: stearic acid, diphenyl guanidine (DPG), tetramethylthiuram disulfide (TMTD), 4,4'-dithiodimorpholine (DTDM), tetrabutylthiuram disulfide (TBTDD), benzothiazyl disulfide (MBTS), hexamethylene-1,6-bisthiosulfate disodium salt dihydrate (sold commercially as DURALINK™ HTS by Flexsys), 2-(morpholinothio) benzothiazole (MBS or MOR), blends of 90% MOR and 10% MBTS (MOR 90), N-tertiarybutyl-2-benzothiazole sulfenamide (TBBS), and N-oxydiethylene thiocarbonyl-N-oxydiethylene sulfonamide (OTOS), zinc 2-ethyl hexanoate (ZEH), and "thioureas".

## 20 Functionalized Elastomer

The nanocomposites of the present invention comprise a blend of a functionalized elastomer and clay, preferably swellable clay, and more preferably exfoliated clay. Elastomers containing such units as *p*-alkylstyrene and other styrenic moieties may be functionalized in accordance with the process of the present invention. Particularly suitable *p*-alkylstyrene containing polymers for functionalization are copolymers of an isoolefin or olefin having from 2 to 7 carbon atoms and a *p*-alkylstyrene, desirably *p*-methylstyrene, as described above. In one embodiment of the present invention it is particularly preferred to use a copolymer of isobutylene and *p*-methylstyrene.

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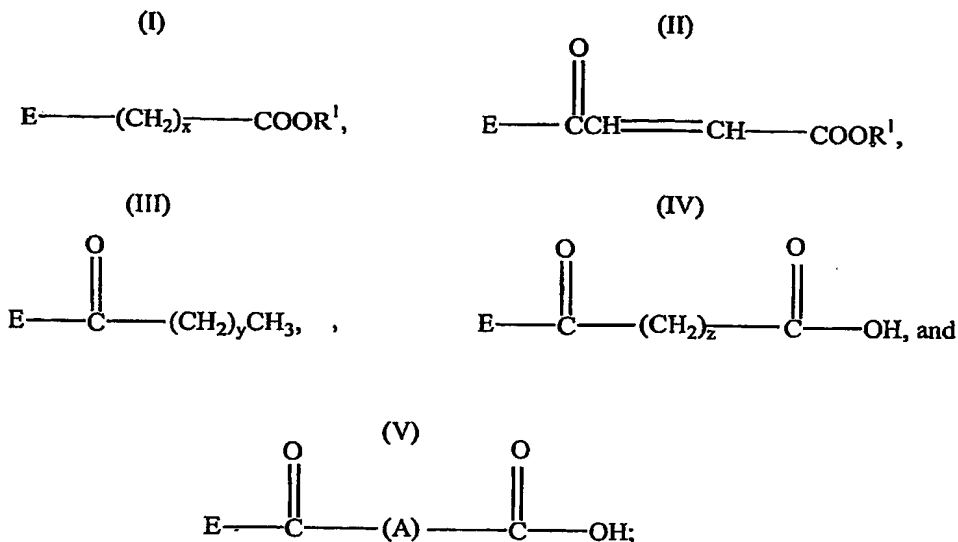
The foregoing elastomers are functionalized by any suitable technique known in the art that will result in the elastomer having a carboxylic acid moiety

or ester moiety pendant to the elastomer polymer chain. In one embodiment, the elastomer is functionalized by reacting the elastomer, such as, for example, butyl rubber and *p*-alkylstyrene containing polymers or copolymers, with a functionalizing compound in the presence of an grafting promoter, either as a melt  
5 or in the presence of a diluent, wherein the functionalizing agent is any suitable agent that will facilitate the creation of a carboxylic acid or ester group pendant to the elastomer. Suitable functionalizing compounds include acid anhydrides, carboxylic acids and acylhalides, typically reacted in the presence of a Lewis acid and the elastomer.

10

For purposes of the present invention, an "grafting promoter" is an element, compound, reagent, blend of compounds, or apparatus (*e.g.*, potentiostat) capable of facilitating the grafting of carboxylic acid and/or ester moieties as described above onto an elastomer, particular, elastomers as described herein.  
15 Non-limiting examples of grafting promoters includes Lewis acids and their equivalents, alkali metals, in particular Li and Na, and alkaline earth metals, in particular Ca.

The functionalized elastomer that results from contacting the grafting  
20 promoter, elastomer and functionalizing compound is an elastomer having one or more carboxylic acid or ester groups pendant to the elastomer backbone. These groups pendant to elastomer, E, may be described by any number of structures, such as described by one or more of the following groups (I), (II), (III), (IV) and (V) pendant to the elastomer, E:



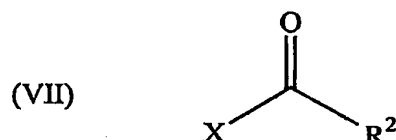
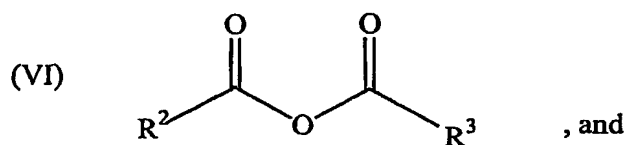
wherein  $\text{R}^1$  is selected from hydrogen,  $\text{C}_1$  to  $\text{C}_{20}$  alkyls, alkenyls or aryls, substituted  $\text{C}_1$  to  $\text{C}_{20}$  alkyls, alkenyls or aryls; wherein the value of  $x$  ranges from 0 to 20, preferably from 1 to 10, and more preferably from 1 to 5; and wherein the value of  $y$  ranged from 0 to 20, preferably from 0 to 10; and wherein the value of  $z$  ranges from 1 to 20, preferably from 1 to 10, and more preferably from 1 to 5; and wherein "A" is an aryl group, either substituted or not.

Preferably,  $\text{R}^1$  is selected from hydrogen,  $\text{C}_1$  to  $\text{C}_6$  alkyls, alkenyls and aryls, substituted  $\text{C}_1$  to  $\text{C}_8$  alkyls, alkenyls and aryls, hydroxyl, and  $\text{C}_1$  to  $\text{C}_8$  alkoxys.

Any part of the elastomer, any monomer unit or any moiety pendant to the elastomer may be functionalized as a result of the functionalization. In one embodiment, the styrenic or substituted styrenic derived unit of the elastomer, when present, is the functionalized monomer unit.

The functionalizing compound includes any compound that will either facilitate the addition or "grafting" of the groups represented by (I) through (V) onto the elastomer of the invention or a compound that itself is grafted onto the

elastomer. In one aspect of the invention, the functionalizing compound is selected from CO<sub>2</sub> and the following (VI) and (VII):



5 wherein R<sup>2</sup> and R<sup>3</sup> are the same or different and are selected from hydrogen, C<sub>1</sub> to C<sub>10</sub> alkyls, alkenyls and aryls, hydroxyl, and C<sub>1</sub> to C<sub>10</sub> alkoxys, wherein R<sup>2</sup> and R<sup>3</sup> may form a ring structure; and wherein X is selected from hydroxyl and halides, preferably bromine and chlorine, and alkoxy groups. Suitable alkoxy groups are such groups as -OCH<sub>3</sub>, -OCH<sub>2</sub>CH<sub>3</sub>, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, -OCH<sub>2</sub>(CH<sub>3</sub>)CH<sub>3</sub>, etc.

10

Non-limiting examples of functionalizing compounds include acid anhydrides and acylhalides. Particularly useful anhydrides include succinic anhydride, maleic anhydride, phthalic anhydride, glutaric anhydride, citraconic anhydride, itaconic anhydride, and other cyclic anhydrides, and mixtures thereof.

15

Particularly useful acylhalides include succinyl chloride, glutaryl chloride, itaconyl chloride, malonyl chloride, adipoyl chloride, diethylmalonyl dichloride, 3-methyladipoyl chloride, pimeloyl chloride, suberoyl chloride, azelaoyl chloride, sebacoyl chloride, isophthaloyl dichloride, phthaloyldichloride, terephthaoyl chloride and mixtures thereof.

20

In one embodiment, the acylhalide will have from 2 to 14 carbon atoms and the acid anhydride will have from 4 to 12 carbon atoms.



A suitable Lewis acid catalyst can be used in preparing the functionalized elastomers; desirable Lewis acid catalysts are based on metals such as boron, aluminum, gallium, indium, titanium, zirconium, tin, arsenic, antimony and  
5 bismuth. Especially preferred are the halide containing compounds of the foregoing metals such as boron trifluoride, aluminum trichloride, aluminum dichloride and the like.

In one embodiment, the functionalization will be carried out in the  
10 presence of a hydrocarbon diluent such as aliphatic hydrocarbons or in the presence of a polar solvent such as carbon disulfide, nitrobenzene, methylene chloride and 1,2 dichloroethane and the like. In another embodiment of the present invention it is desirable to carry out the process as a melt blend at a temperature wherein the elastomer exists as a molten or semi-molten state, or  
15 from 0 to 200°C in one embodiment, and from 20 to 180°C in another embodiment.

The functionalization of the polymers typically is carried out at temperatures of from -50°C to 150 °C, for times sufficient to add the functional  
20 group, that is, the alkyl carbonyl, alkenyl carboxylic acid, to the aromatic ring of the *p*-alkylstyrene containing polymer.

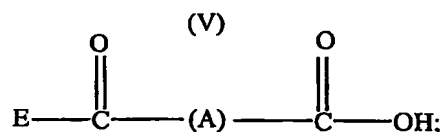
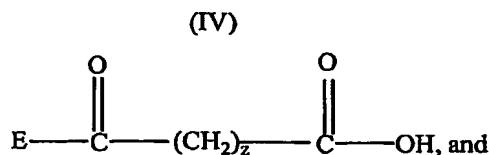
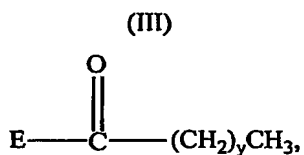
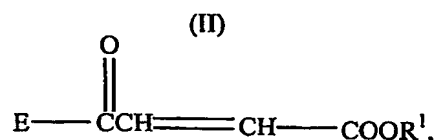
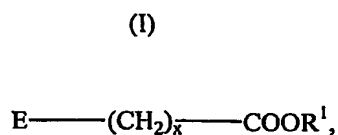
The ratio of functionalizing compound, such as the acylhalide or acid anhydride, to the styrenic units in the *p*-alkylstyrene containing polymer can vary  
25 widely. In general, however, from 0.01 to 10 moles of acylhalide or acid anhydride or unsaturated anhydride per 1 mole of styrenic moieties in the styrene containing polymer will be employed.

For elastomers containing *p*-methylstyrene, the benzyl group can be  
30 oxidized in the presence of an oxidizing agent to produce carboxylic acid on the elastomer (structure I, X = O). In another embodiment the benzyl group can react with an alkali metal such as Li, then CO<sub>2</sub> with protonation to produce carboxylic

acid on the elastomer (structure I,  $X = 0$ ). Both of these functional polymers can also be used for the nanocomposite preparation disclosed herein.

The functional groups "grafted" onto the elastomer backbone may be present from 0.01 wt% to 15 wt%, by weight of the grafted functionalized (or "grafted") elastomer in one embodiment, and from 0.05 wt% to 10 wt% in another embodiment, and from 0.1 wt% to 8 wt% in yet another embodiment.

One aspect of the invention just described is a nanocomposite comprising clay and an elastomer comprising  $C_2$  to  $C_{10}$  olefin derived units; wherein the elastomer comprises functionalized monomer units described by the following groups (I), (II), (III), (IV) and (V) pendant to the elastomer, E:



wherein  $R^1$  is selected from hydrogen,  $C_1$  to  $C_{20}$  alkyls, alkenyls or aryls, substituted  $C_1$  to  $C_{20}$  alkyls, alkenyls or aryls; wherein the value of  $x$  ranges from 0 to 20, preferably from 1 to 10, and more preferably from 1 to 5; and wherein the value of  $y$  ranged from 0 to 20, preferably from 0 to 10; and wherein the value of  $z$  ranges from 1 to 20, preferably from 1 to 10, and more preferably from 1 to 5; and wherein "A" is an aryl group, either substituted or not.

Alternately, the nanocomposite of the invention can be described as comprising clay and the reaction product of contacting an elastomer comprising C<sub>2</sub> to C<sub>10</sub> olefin derived units, a grafting promoter and at least one functionalizing compound. The product of contacting the elastomer and the functionalizing compound and grafting promoter may be described as an elastomer having one or more carboxylic acid and (or) an ester moieties pendant to the elastomer in one embodiment, or described as any one or more of structures (I) through (IV) above. The amount of functionalization (or number of functionalized units) is from 0.01 wt% to 15 wt% in one embodiment, and other ranges as described herein.

10

In one embodiment of the invention, the elastomer also comprises styrene derived units, alkylstyrene derived units in one embodiment, *p*-alkylstyrene derived units in another embodiment. In another embodiment, the elastomer comprises a group selected from  $\alpha$ -methylstyrene, *o*-methylstyrene, *m*-methylstyrene, and *p*-methylstyrene units. In yet another embodiment, the elastomer is poly(isobutylene-*co-p*-methylstyrene). And in yet another embodiment, the elastomer is a terpolymer comprising ethylene derived units, propylene derived units, and styrene derived units. And in yet another embodiment, the elastomer is a terpolymer comprising ethylene derived units, propylene derived units, and *p*-methylstyrene derived units. When present, the elastomer comprises from 1 wt% to 15 wt% by weight of the elastomer of the *p*-alkylstyrene derived unit, *p*-methylstyrene in one embodiment.

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In another embodiment, the elastomer also comprises monomer units selected from styrenic derived units and substituted styrenic derived units.

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In yet another embodiment of the elastomer, the olefin is selected from one or more of isobutylene, isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 4-methyl-1-pentene, ethylene, propene, 1-butene, 1-hexene, and 1-octene.

30

In yet another embodiment of the elastomer, the styrene derived units are present from 1 to 15 wt% of the elastomer when present.

5 In yet another embodiment of the elastomer, the elastomer comprises *p*-methylstyrene derived units.

In yet another embodiment of the elastomer, the elastomer also comprises isoolefin derived units and *p*-methylstyrene derived units.

10 In yet another embodiment of the elastomer, the elastomer also comprises multiolefin derived units.

In one embodiment of the invention, the functionalized units are present on the elastomer from 0.01 wt% to 15 wt% of the elastomer.

15

In yet another embodiment, the elastomer is selected from any one or a mixture of natural rubber, poly(isobutylene-*co*-isoprene), polybutadiene, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene), poly(styrene-isoprene-butadiene), star-branched polyisobutylene rubber, poly(isobutylene-*co-p*-methylstyrene), ethylene-propylene-alkylstyrene rubber, ethylene-propylene-styrene rubber; and from any one or a mixture of poly(isobutylene-*co*-isoprene), polybutadiene, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene), poly(styrene-isoprene-butadiene), star-branched polyisobutylene rubber, poly(isobutylene-*co-p*-methylstyrene), ethylene-propylene-alkylstyrene rubber, ethylene-propylene-styrene rubber in another embodiment.

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In one embodiment, the clay is swellable, and exfoliated in another embodiment, wherein the clay has been treated with an exfoliating agent to form an exfoliated clay. In the embodiment where the clay is exfoliated, the exfoliating agent may be selected from ammonium ion, alkylamines, alkylammonium ion (primary, secondary, tertiary and quaternary), phosphonium or sulfonium

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derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines and sulfides and blends thereof.

The clay is present from 0.1 wt% to 50 wt% of the nanocomposite in one  
5 embodiment; and present from 0.5 wt% to 15 wt% of the nanocomposite in  
another embodiment; and present from 1 wt% to 30 wt% of the nanocomposite in  
yet another embodiment.

The nanocomposite may also comprise other components such as a filler  
10 selected from carbon black, modified carbon black, silica, precipitated silica, and  
blends thereof.

Further, the nanocomposite may also comprise one or more curing agents,  
wherein the curing agent is selected from zinc, zinc stearate, fatty acids, sulfur,  
15 diamine, diepoxy, polyamine, polyepoxy and mixtures thereof.

Further, the nanocomposite may also comprise a secondary rubber or  
"general purpose rubber", the secondary rubber selected from natural rubber,  
polybutadiene rubber, nitrile rubber, silicon rubber, polyisoprene rubber,  
20 poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene) rubber, styrene-  
isoprene-butadiene rubber, ethylene-propylene rubber, brominated butyl rubber,  
chlorinated butyl rubber, halogenated isoprene, halogenated isobutylene  
copolymers, polychloroprene, star-branched polyisobutylene rubber, star-branched  
brominated butyl rubber, poly(isobutylene-*co*-isoprene) rubber; halogenated  
25 poly(isobutylene-*co-p*-methylstyrene), ethylene-propylene rubber and mixtures  
thereof.

In one aspect of the invention, the nanocomposite is formed using any  
suitable method known in the art into an air barrier such as an innerliner or  
30 innertube suitable for vehicle tires, truck tires, automotive and motorcycle tires,  
and other tires.

The invention also includes a method of forming a nanocomposite comprising contacting clay, an elastomer, an grafting promoter, and at least one functionalizing compound, wherein the elastomer comprises C<sub>2</sub> to C<sub>10</sub> olefin derived units.

5

In one embodiment, the elastomer is first contacted with the functionalizing compound, followed by contacting with the clay. In another embodiment, the elastomer, clay and acid functionalizing compound are contacted simultaneously.

10

In one embodiment, the grafting promoter is a Lewis acid selected from halide and alkyl containing compounds of boron, aluminum, gallium, indium, titanium, zirconium, tin, arsenic, antimony and bismuth, and mixtures thereof.

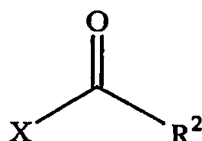
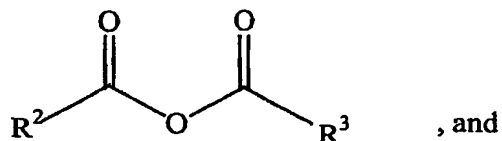
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In yet another embodiment, the method comprises contacting a diluent selected from carbon disulfide, nitrobenzene, methylene chloride, 1,2 dichloroethane, hexane, cyclohexane and mixtures thereof.

In yet another embodiment, the elastomer and functionalizing compound are melt blended, thus forming the functionalized elastomer.

20

In one embodiment, functionalizing compound is selected from CO<sub>2</sub> and the following structures:



wherein  $\text{R}^2$  and  $\text{R}^3$  are the same or different and are selected from hydrogen,  $\text{C}_1$  to  $\text{C}_{10}$  alkyls, alkenyls and aryls, hydroxyl, and  $\text{C}_1$  to  $\text{C}_{10}$  alkoxys, wherein  $\text{R}^2$  and  $\text{R}^3$  may form a ring structure; and wherein X is selected from hydroxyl and halides, preferably bromine and chlorine, and alkoxy groups. In another embodiment,  $\text{R}_2$  and  $\text{R}_3$  are the same or different and are selected from hydrogen,  $\text{C}_1$  to  $\text{C}_8$  alkyls, alkenyls and aryls, wherein  $\text{R}_2$  and  $\text{R}_3$  may form 4 to 6 member ring structures such as maleic anhydride, succinic anhydride, phthalic anhydride and substituted derivatives thereof.

The following examples illustrate the invention:

### TEST METHODS

*Permeability Testing.* All specimens were compression molded with slow cooling to provide defect free pads. A compression and curing press was used for rubber samples. Typical thickness of a compression molded pad is about 15 mil. using an Arbor press, 2" diameter disks were then punched out from molded pads for permeability testing. These disks were conditioned in a vacuum oven at  $60^\circ\text{C}$  overnight prior to the measurement. The oxygen permeation measurements were done using a Mocon OX-TRAN 2/61 permeability tester at  $40^\circ\text{C}$  under the principle of R. A. Pasternak et. al. in 8 JOURNAL OF POLYMER SCIENCE: PART A-2 467 (1970). Disks thus prepared were mounted on a template and sealed with a vacuum grease. 10 psi nitrogen was kept on one side of the disk, whereas the other

side is 10 psi oxygen. Using the oxygen sensor on the nitrogen side, increase in oxygen concentration on the nitrogen side with time could be monitored. The time required for oxygen to permeate through the disk, or for oxygen concentration on the nitrogen side to reach a constant value, is recorded and used  
5 to determine the oxygen permeability.

*XRD Measurement.* The average d-spacing between clay plates in the final composite is measured by standard small angle X-Ray Instrumentation using 2D Area Detector System. The scan range is 0 to 10°, 2θ and collection time of 900  
10 seconds.

#### EXAMPLES

The present invention, while not meant to be limiting by, may be better understood by reference to the following example and Tables.  
15

As a comparative example (Example 1), the permeability of poly(isobutylene-co-p-methylstyrene) ("XP 50") comprising 11.5 wt% p-methylstyrene units by weight of the polymer was measured. The permeability data are summarized in Table 2.

20

In example 2, the elastomer XP-50 containing 11.5 wt% p-methylstyrene (55 g) and succinic anhydride (3g) were dissolved in methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>). To the solution was added AlCl<sub>3</sub> (8 g). After being stirred for 1.5 hours, the solution was poured into methanol containing 120 mmol HCl to afford  
25 the functionalized elastomer. Next, the functionalized elastomer (40.5 g) was melt blended in a Brabender at 160°C, followed by addition of Cloisite 6A clay (4.5 g) and mixing for 10 min. A sample of this composition was pressed into a film tested for permeability. These data are summarized in Table 2. An unpressed sample was measured for d-spacings. The clay d-spacings from XRD  
30 measurements was 5.04 nm.



Thus the d-spacing of clay in nanocomposite (Example 2) is much larger than that (3.60 nm) of original Cloisite 6A. The significant increase of the clay d-spacing after nanocomposite formation indicates a strong intercalant or exfoliation took place.

5

For Example 3, XP 50 containing 11.5 % *p*-methylstyrene (55 g) and succinic anhydride (1.0 g) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>. To this solution was added AlCl<sub>3</sub> (2.7 g). After being stirred for 1.5 hours, the solution was poured into methanol containing 100 mmol HCl and the obtained product was washed with acetone and dried under vacuum overnight. Next, the modified product was melt blended in a Brabender at 160 °C and mixed with 4.5 g of clay (Cloisite 6A) for 10 minutes at a rotor speed of 60 rpm. A sample of this composition was tested for permeability, data for which is summarized in Table 2.

15 For Example 4, XP 50 containing 11.5 % *p*-methylstyrene (75 g) and succinic anhydride (1.03 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. To this solution was added AlCl<sub>3</sub> (2.8 g). After being stirred for 1.5 hours, the solution is poured into methanol containing 100 mmol HCl and the obtained product was washed with acetone and dried under vacuum overnight. Then the functionalized elastomer was melt blended in a Brabender at 160 °C and mixed with 4.5 g of clay (Cloisite 6A) for 10 minutes at a rotor speed of 60 rpm. A sample of this composition was tested for permeability and, data for which is summarized in Table 2.

25 Example 5 illustrates the use of functionalized polymer in blend application. For example 5, the following procedure was carried out: Butyl rubber (XP50, 31.5 grams) and modified butyl (9.0 grams) from example 2 were melt in Brabender for three minutes with a rotor speed of 60 rpm at 160 °C. To the melt was added Cloisite 6A (4.5 grams). The mixture was further mixed for 10 minutes. A sample of this composition was tested for permeability and, data for which is summarized in Table 2.

30

Nanocomposites of the present invention have a permeation coefficient of less than 7 mm·cc/(m<sup>2</sup>·day·mmHg) at 40°C in one embodiment, and less than 6 mm·cc/(m<sup>2</sup>·day·mmHg) at 40°C in another embodiment, and less than 5 mm·cc/(m<sup>2</sup>·day·mmHg) at 40°C in yet another embodiment, and between 2 and 7  
5 mm·cc/(m<sup>2</sup>·day·mmHg) at 40°C in yet another embodiment.

While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to many different variations not  
10 illustrated herein. For these reasons, then, reference should be made solely to the appended claims for purposes of determining the scope of the present invention. Further, certain features of the present invention are described in terms of a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges formed by any combination of these limits are within the  
15 scope of the invention unless otherwise indicated.

All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted. Further, all documents cited herein, including testing procedures, are herein fully incorporated by  
20 reference for all jurisdictions in which such incorporation is permitted.

**Table 1. Material Description**

<b>Component</b>	<b>Description</b>	<b>Material Source</b>
maleic anhydride	"functionalizing compound"	Aldrich Chemical Company
methylene chloride	CH <sub>2</sub> Cl <sub>2</sub>	Aldrich Chemical Company
succinic anhydride	"functionalizing compound"	Aldrich Chemical Company
6A	Montmorillonite clay treated with di-methyl di-hydrogenated tallow alkyl ammonia chloride	Cloisite 6A, Southern Clay

TABLE 2. Permeability data<sup>1</sup>

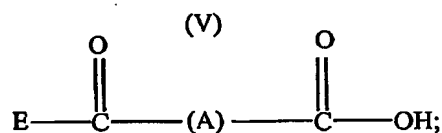
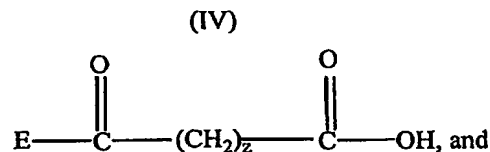
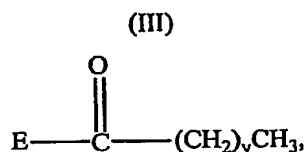
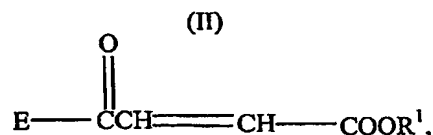
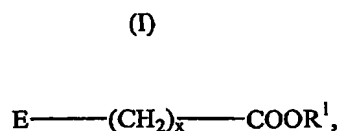
Example	functionalizing compound (grams)	grafted functional unit (wt% relative to elastomer)	permeation coefficient (mm·cc/(m <sup>2</sup> ·day·mm Hg)) at 40°C
1 (comp.)	-	-	7.67
2	succinic anhydride (3.0 g)	2.4	3.60
3	succinic anhydride (1.0 g)	0.71	3.85
4	succinic anhydride (1.03 g)	0.48	4.46
5	--	--	5.70

5 1. all samples were dried under vacuum prior to permeation measurements.

## CLAIMS

We claim:

1. A nanocomposite comprising clay and an elastomer comprising C<sub>2</sub> to C<sub>10</sub> olefin derived units; wherein the elastomer also comprises functionalized monomer units described by the following groups (I), (II), (III), (IV) and (V) pendant to the elastomer, E:



- wherein R<sup>1</sup> is selected from hydrogen, C<sub>1</sub> to C<sub>20</sub> alkyls, alkenyls or aryls, substituted C<sub>1</sub> to C<sub>20</sub> alkyls, alkenyls or aryls; wherein the value of x ranges from 0 to 20, preferably from 1 to 10, and more preferably from 1 to 5; and wherein the value of y ranged from 0 to 20, preferably from 0 to 10; and wherein the value of z ranges from 1 to 20, preferably from 1 to 10, and more preferably from 1 to 5; and wherein "A" is an aryl group, either substituted or not.

2. The nanocomposite of Claim 1, wherein the elastomer also comprises monomer units selected from styrenic derived units and substituted styrenic derived units.

3. The nanocomposite of Claim 2, wherein the styrenic units are functionalized.
4. The nanocomposite of Claim 1, wherein the elastomer is not halogenated.
- 5 5. The nanocomposite of Claim 1, wherein the olefin is selected from one or more of isobutylene, isobutene, isoprene, cyclopentadiene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 4-methyl-1-pentene, ethylene, propene, 1-butene, 1-hexene, and 1-octene.
- 10 6. The nanocomposite of Claim 2, wherein the styrene derived units are present from 1 to 15 wt% of the elastomer.
- 15 7. The nanocomposite of Claim 1, wherein the elastomer comprises *p*-methylstyrene derived units.
8. The nanocomposite of Claim 1, wherein the elastomer also comprises isoolefin derived units and *p*-methylstyrene derived units.
- 20 9. The nanocomposite of Claim 1, wherein the elastomer also comprises multiolefin derived units.
10. The nanocomposite of Claim 1, wherein the elastomer is selected from any one or a mixture of natural rubber, poly(isobutylene-*co*-isoprene),  
25 polybutadiene, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene), poly(styrene-isoprene-butadiene), star-branched polyisobutylene rubber, poly(isobutylene-*co-p*-methylstyrene), ethylene-propylene-alkylstyrene rubber, ethylene-propylene-styrene rubber.
- 30 11. The nanocomposite of Claim 1, wherein the functionalized units are present on the elastomer from 0.01 wt% to 15 wt% of the elastomer.

12. The nanocomposite of Claim 1, wherein the clay has been treated with an exfoliating agent to form an exfoliated clay.
13. The nanocomposite of Claim 12, wherein the exfoliating agent is selected from ammonium ion, alkylamines, alkylammonium ion (primary, secondary, tertiary and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines and sulfides and blends thereof.
14. The nanocomposite of Claim 1, wherein the clay is present from 0.1 wt% to 50 wt% of the nanocomposite.
15. The nanocomposite of Claim 1, wherein the clay is present from 0.5 wt% to 15 wt% of the nanocomposite.
16. The nanocomposite of Claim 1, also comprising a filler selected from carbon black, modified carbon black, silica, precipitated silica, and blends thereof.
17. The nanocomposite of Claim 1, also comprising one or more curing agents.
18. The nanocomposite of Claim 17, wherein the curing agent is selected from zinc, zinc stearate, fatty acids, sulfur, diamine, diepoxy, polyamine, polyepoxy and mixtures thereof.
19. The nanocomposite of Claim 1, also comprising a secondary rubber selected from natural rubber, polybutadiene rubber, nitrile rubber, silicon rubber, polyisoprene rubber, poly(styrene-co-butadiene) rubber, poly(isoprene-co-butadiene) rubber, styrene-isoprene-butadiene rubber, ethylene-propylene rubber, brominated butyl rubber, chlorinated butyl rubber, halogenated isoprene, halogenated isobutylene copolymers,

polychloroprene, star-branched polyisobutylene rubber, star-branched brominated butyl rubber, poly(isobutylene-*co*-isoprene) rubber; halogenated poly(isobutylene-*co*-*p*-methylstyrene), ethylene-propylene rubber and mixtures thereof.

5

20. A tire innerliner comprising the nanocomposite of Claim 1.

21. An innertube comprising the nanocomposite of Claim 1.

10 22. A method of forming a nanocomposite comprising contacting clay, an elastomer, an grafting promoter, and at least one functionalizing compound, wherein the elastomer comprises C<sub>2</sub> to C<sub>10</sub> olefin derived units.

15 23. The method of Claim 22, wherein the elastomer is first contacted with the functionalizing compound, followed by contacting with the clay.

24. The method of Claim 22, wherein the elastomer, clay and acid functionalizing compound are contacted simultaneously.

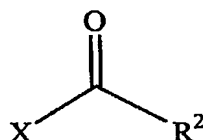
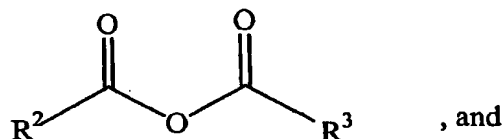
20 25. The method of Claim 22, wherein the grafting promoter is a Lewis acid selected from halide and alkyl containing compounds of boron, aluminum, gallium, indium, titanium, zirconium, tin, arsenic, antimony and bismuth, and mixtures thereof.

25 26. The method of Claim 22, further comprising contacting a diluent selected from carbon disulfide, nitrobenzene, methylene chloride, 1,2 dichloroethane, hexane, cyclohexane and mixtures thereof.

30 27. The method of Claim 22, wherein the elastomer and functionalizing compound are melt blended.



28. The method of Claim 22, wherein the functionalizing compound is selected from CO<sub>2</sub> and the following:



5 wherein R<sup>2</sup> and R<sup>3</sup> are the same or different and are selected from hydrogen, C<sub>1</sub> to C<sub>10</sub> alkyls, alkenyls and aryls, hydroxyl, and C<sub>1</sub> to C<sub>10</sub> alkoxys, wherein R<sup>2</sup> and R<sup>3</sup> may form a ring structure; and wherein X is selected from hydroxyl, halides, preferably bromine and chlorine, and alkoxy groups.

- 10 29. The method of Claim 22, wherein the functionalizing compound is selected from succinic anhydride, maleic anhydride, phthalic anhydride, glutaric anhydride, citraconic anhydride, itaconic anhydride, and other cyclic anhydrides, succinyl chloride, glutaryl chloride, itaconyl chloride, malonyl chloride, adipoyl chloride, diethylmalonyl dichloride, 3-methyladipoyl chloride, pimeloyl chloride, suberoyl chloride, azelaoyl chloride, sebacoyl chloride, isophthaloyl dichloride, phthaloyldichloride, terephthaoyl chloride.

- 20 30. The method of Claim 22, wherein the elastomer also comprises monomer units selected from styrenic derived units and substituted styrenic derived units.

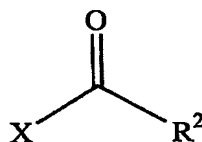
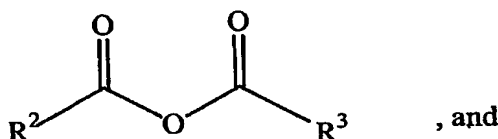
31. The method of Claim 22, wherein the olefin is selected from one or more of isobutylene, isobutene, isoprene, cyclopentadiene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 4-methyl-1-pentene, ethylene, propene, 1-butene, 1-hexene, and 1-octene.
- 5 32. The method of Claim 30, wherein the styrene derived units are present from 1 to 15 wt% of the elastomer.
- 10 33. The method of Claim 22, wherein the elastomer comprises *p*-methylstyrene derived units.
34. The method of Claim 22, wherein the elastomer also comprises isoolefin derived units and *p*-methylstyrene derived units.
- 15 35. The method of Claim 22, wherein the elastomer also comprises multiolefin derived units.
- 20 36. The method of Claim 22, wherein the elastomer is selected from any one or a mixture of natural rubber, poly(isobutylene-*co*-isoprene), polybutadiene, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene), poly(styrene-isoprene-butadiene), star-branched polyisobutylene rubber, poly(isobutylene-*co*-*p*-methylstyrene), ethylene-propylene-alkylstyrene rubber, ethylene-propylene-styrene rubber.
- 25 37. The method of Claim 22, wherein the elastomer is functionalized by contacting with the functionalizing compound, wherein the functional groups are present on the elastomer from 0.01 wt% to 15 wt% of the elastomer.
- 30 38. The method of Claim 22, wherein the clay has been treated with an exfoliating agent to form an exfoliated clay.

39. The method of Claim 38, wherein the exfoliating agent is selected from ammonium ion, alkylamines, alkylammonium ion (primary, secondary, tertiary and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines and sulfides and blends thereof.
40. The method of Claim 22, wherein the clay is present from 0.1 wt% to 50 wt% of the nanocomposite.
41. The method of Claim 22, wherein the clay is present from 0.5 wt% to 15 wt% of the nanocomposite.
42. The method of Claim 22, also comprising a filler selected from carbon black, modified carbon black, silica, precipitated silica, and blends thereof.
43. The method of Claim 22, also comprising one or more curing agents.
44. The method of Claim 43, wherein the curing agent is selected from zinc, zinc stearate, fatty acids, sulfur, diamine, diepoxy, polyamine, polyepoxy and mixtures thereof.
45. The method of Claim 22, also comprising a secondary rubber selected from natural rubber, polybutadiene rubber, nitrile rubber, silicon rubber, polyisoprene rubber, poly(styrene-co-butadiene) rubber, poly(isoprene-co-butadiene) rubber, styrene-isoprene-butadiene rubber, ethylene-propylene rubber, brominated butyl rubber, chlorinated butyl rubber, halogenated isoprene, halogenated isobutylene copolymers, polychloroprene, star-branched polyisobutylene rubber, star-branched brominated butyl rubber, poly(isobutylene-co-isoprene) rubber; halogenated poly(isobutylene-co-p-methylstyrene), ethylene-propylene rubber and mixtures thereof.
46. A tire innerliner made by the method of Claim 22.

47. An innertube made by the method of Claim 22.

48. A nanocomposite comprising clay and the reaction product of contacting  
5 an elastomer comprising C<sub>2</sub> to C<sub>10</sub> olefin derived units, an grafting promoter, and at least one functionalizing compound.

49. The nanocomposite of Claim 48, wherein the functionalizing compound is selected from CO<sub>2</sub> and the following:



10

wherein R<sup>2</sup> and R<sup>3</sup> are the same or different and are selected from hydrogen, C<sub>1</sub> to C<sub>10</sub> alkyls, alkenyls and aryls, hydroxyl, and C<sub>1</sub> to C<sub>10</sub> alkoxys, wherein R<sup>2</sup> and R<sup>3</sup> may form a ring structure; and wherein X is  
15 selected from hydroxyl, halides, preferably bromine and chlorine, and alkoxy groups.

50. The nanocomposite of Claim 48, wherein the functionalizing compound is selected from succinic anhydride, maleic anhydride, phthalic anhydride, glutaric anhydride, citraconic anhydride, itaconic anhydride, and other  
20 cyclic anhydrides, succinyl chloride, glutaryl chloride, itaconyl chloride, malonyl chloride, adipoyl chloride, diethylmalonyl dichloride, 3-methyladipoyl chloride, pimeloyl chloride, suberoyl chloride, azelaoyl

chloride, sebacoyl chloride, isophthaloyl dichloride, phthaloyldichloride, terephthaoyl chloride.

51. The nanocomposite of Claim 48, wherein the grafting promoter is a Lewis  
5 acid selected from halide and alkyl containing compounds of boron, aluminum, gallium, indium, titanium, zirconium, tin, arsenic, antimony and bismuth, and mixtures thereof.
52. The nanocomposite of Claim 48, wherein the components are contacted in  
10 a diluent selected from carbon disulfide, nitrobenzene, methylene chloride, 1,2 dichloroethane, hexane, cyclohexane and mixtures thereof.
53. The nanocomposite of Claim 48, wherein the elastomer also comprises  
15 monomer units selected from styrenic derived units and substituted styrenic derived units.
54. The nanocomposite of Claim 53, wherein the styrenic units are functionalized.
- 20 55. The nanocomposite of Claim 48, wherein the elastomer is not halogenated.
56. The nanocomposite of Claim 48, wherein the olefin is selected from one or  
more of isobutylene, isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 4-methyl-1-pentene, ethylene, propene, 1-butene, 1-  
25 hexene, and 1-octene.
57. The nanocomposite of Claim 53, wherein the styrene derived units are present from 1 to 15 wt% of the elastomer.
- 30 58. The nanocomposite of Claim 48, wherein the elastomer comprises *p*-methylstyrene derived units.

59. The nanocomposite of Claim 48, wherein the elastomer also comprises isoolefin derived units and *p*-methylstyrene derived units.
60. The nanocomposite of Claim 48, wherein the elastomer also comprises multiolefin derived units.
61. The nanocomposite of Claim 48, wherein the elastomer is selected from any one or a mixture of natural rubber, poly(isobutylene-*co*-isoprene), polybutadiene, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene), poly(styrene-isoprene-butadiene), star-branched polyisobutylene rubber, poly(isobutylene-*co-p*-methylstyrene), ethylene-propylene-alkylstyrene rubber, ethylene-propylene-styrene rubber.
62. The nanocomposite of Claim 48, wherein the functionalized derived units are present on the elastomer from 0.01 wt% to 15 wt% of the elastomer.
63. The nanocomposite of Claim 48, wherein the clay has been treated with an exfoliating agent to form an exfoliated clay.
64. The nanocomposite of Claim 63, wherein the exfoliating agent is selected from ammonium ion, alkylamines, alkylammonium ion (primary, secondary, tertiary and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines and sulfides and blends thereof.
65. The nanocomposite of Claim 48, wherein the clay is present from 0.1 wt% to 50 wt% of the nanocomposite.
66. The nanocomposite of Claim 48, wherein the clay is present from 0.5 wt% to 15 wt% of the nanocomposite.

67. The nanocomposite of Claim 48, also comprising a filler selected from carbon black, modified carbon black, silica, precipitated silica, and blends thereof.
- 5 68. The nanocomposite of Claim 48, also comprising one or more curing agents.
69. The nanocomposite of Claim 68, wherein the curing agent is selected from zinc, zinc stearate, fatty acids, sulfur, diamine, diepoxy, polyamine, polyepoxy and mixtures thereof.
- 10
70. The nanocomposite of Claim 48, also comprising a secondary rubber selected from natural rubber, polybutadiene rubber, nitrile rubber, silicon rubber, polyisoprene rubber, poly(styrene-*co*-butadiene) rubber, poly(isoprene-*co*-butadiene) rubber, styrene-isoprene-butadiene rubber, ethylene-propylene rubber, brominated butyl rubber, chlorinated butyl rubber, halogenated isoprene, halogenated isobutylene copolymers, polychloroprene, star-branched polyisobutylene rubber, star-branched brominated butyl rubber, poly(isobutylene-*co*-isoprene) rubber; halogenated poly(isobutylene-*co*-*p*-methylstyrene) and mixtures thereof.
- 15
- 20
71. A tire innerliner comprising the nanocomposite of Claim 48.
72. An innertube comprising the nanocomposite of Claim 48.

## FUNCTIONALIZED ELASTOMER NANOCOMPOSITE

### ABSTRACT

An embodiment of the present invention is a nanocomposite comprising a clay and an elastomer comprising at least C<sub>2</sub> to C<sub>10</sub> olefin derived units; wherein the elastomer also comprises functionalized monomer units pendant to the elastomer. Desirable embodiments of the elastomer include poly(isobutylene-*co*-*p*-alkylstyrene) elastomers and poly(isobutylene-*co*-isoprene) elastomers, which are functionalized via Friedel-Crafts reaction with a Lewis acid and a functionalizing agent such as acid anhydrides and/or acylhalides. The clay is exfoliated in one embodiment by the addition of exfoliating agents such as alkyl amines and silanes to the clay. The composition can include secondary rubbers such as general purpose rubbers, and curatives, fillers, and the like. The nanocomposites of the invention have improved air barrier properties such as are useful for tire innerliners and innertubes.